

## AMPHOTERIC BEHAVIOR OF COMPLEX SYSTEMS.

### IV. NOTE ON THE ISOELECTRIC POINT AND IONIZATION CONSTANTS OF SULFANILIC ACID.\*

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In the experiments described in the preceding papers the assumption was made that sulfanilic acid was an ampholyte. While its formula would tend to justify such an assumption, there seems to be no record of any determinations of its basic ionization constant or of its isoelectric point. It is to be expected that the magnitude of the former is very small and that the isoelectric point will be at a very low pH.

Titration methods do not offer a satisfactory method of attack since the pH at which basic neutralization commences is so low that a small change in E.M.F. corresponds to a relatively large difference in hydrogen ion concentration, and moreover the hydrogen ion concentration change is not a measure of salt formation in such a region of pH. Also the large acid ionization constant of the sulfanilic acid tends to "cover" or mask any small basic neutralization.

Solubilities were therefore determined in water and in various concentrations of hydrochloric acid. Table I gives results at 24°C., which are typical. The first eight columns give the molalities of the substances named. The basic ion from the sulfanilic acid is called  $S^+$ , and the acid ion  $S^-$ .  $K$ , in Column 9, is the function 
$$\frac{(H^+) \left( \frac{\text{unionized}}{\text{sulfanilic}} \right)}{(\text{salt})}$$
. The degree of hydrolysis,  $h$ , is calculated for a salt concentration equal to the concentration of HCl corresponding to its place in the table.

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Values of  $h$  are calculated by taking a total salt concentration equal to the corresponding hydrochloric acid concentration and, using the value of  $K$  in Column 9, solving for the concentration of unhydrolyzed

TABLE I.

1	2	3	4	5*	6†	7	8‡	9§	10	11
HCl	$H^+ \times 10^3$	$OH^- \times 10^{14}$	Solubility of sulfanilic acid	$S^- \times 10^4$	$S^+ \times 10^4$	Unionized sulfanilic acid	Salt $\times 10^3$	K	h	$K_b \times 10^{13}$
.00	.67	15.	.0715	56.	.93	.0648	—	—	—	—
.05	4.7	2.1	.0664	9.8	6.3	.0648	—	—	—	—
.07	6.5	1.54	.0661	7.0	8.5	.0646	—	—	—	—
.08	7.4	1.35	.0663	6.2	9.6	.0647	—	—	—	—
.087	8.0	1.25	.0665	5.8	10.5	.0649	—	—	—	—
.10	9.2	1.08	.0675	5.1	—	—	1.72	3.46	.97	2.6
.25	22.5	.44	.0689	2.1	—	—	3.77	3.92	.948	2.3
.50	42.	.24	.0709	1.2	—	—	5.9	4.6	.923	1.8
									(.914)	(2.1)
.85	68.	.147	.0714	.73	—	—	6.5	6.75	.917	1.2
									(.874)	(1.95)
Mean.....						.06476				
1.			.0713							
1.3			.0705							
1.8			.0668							
2.			.0659							
2.5			.0645							
4.			.058							
6.			.051							

\* Using the value  $7 \times 10^{-4}$  for the acid ionization constant.

† Using the value  $2 \times 10^{-15}$  for the basic ionization constant.

‡ Obtained by subtracting the mean of the values in Column 7 plus twice the respective values in Column 5 from the values in Column 4.

§ The indicated function of the values in Columns 2 and 8 with the mean of those in Column 7.

|| The values in parentheses are obtained by putting  $K$  (Column 9) equal to 4.0. See text.

chloride. We are in such a pH region, however, that though we can neglect the acid ionization of sulfanilic acid, we cannot neglect the ionization of the HCl formed by hydrolysis; so that, since the hydrolysis is in all cases large, the measured value of the hydrogen ion con-

centration for the corresponding molality of HCl is substituted in the formula rather than the total concentration of the HCl formed by hydrolysis.

It will be noted that the values of  $K$  in Column 9 regularly increase. This is due to the fact that at higher concentrations of HCl the actual solubility of the sulfanilic acid decreases rapidly as the HCl concentration increases, as shown in Table I. At these higher HCl concentrations we are in such a pH region that the thermodynamic environment of the solvent changes rapidly with comparatively small changes in the ratio of the hydrogen ion concentration. For this reason it is thought that a value of about 4.0 for  $K$  in Column 9 is probably not far from correct, and the corresponding values of  $h$  and  $K_b$  are accordingly given in parentheses.

An approximate check on the magnitude of  $K_b$  can be obtained by noting the fact that there is a point of minimum solubility which comes apparently between cH values 0.047 and 0.065. Using the well known Michaelis relation, and the value  $7 \times 10^{-4}$  for  $K_a$ ,  $K_b$  is found to lie between 1.7 and  $3.2 \times 10^{-15}$ .

#### *Other Constants Used in the Series.*

From the titration curves in Paper II of this series the pH at which any fraction of glycine or sulfanilic acid is neutralized may be read. This permits a calculation of their ionization constants, values of which are given in Table II.

These values are in good agreement with those given by Scudder (1) for glycine. The curve for sulfanilic acid did not permit as satisfactory reading, and since the literature gives values which seem to vary somewhat, the following determination of the acid ionization constant of sulfanilic acid was made. The method was to take conductivity ratios at different known concentrations. Since conductivities are additive, their ratios will be a measure of the ratios of the sulfonate ion concentrations at respective total acid concentrations. Thus if  $X$  be the concentration of sulfanilic ion (and also of hydrogen ion) at total concentration  $C$ , and  $X'$  be their concentrations at total concentration  $C'$ , then  $X' = rX$ , where  $r$  is the ratio of the conductivities at concentrations  $C$  and  $C'$ .

TABLE II.

Ion/molecule ratio	Glycine				Sulfanilic acid	
	$cOH \times 10^{12}$	$K_b \times 10^{12}$	$cH \times 10^{10}$	$K_a \times 10^{10}$	$cH \times 10^4$	$K_a \times 10^4$
1 : 3	6.45	2.15	6.6	2.2	—	—
1 : 2	4.26	2.13	4.46	2.23	14.1	7.05
1 : 1	2.24	2.24	2.24	2.24	7.24	7.24
2 : 1	1.1	2.2	1.15	2.3	—	—
3 : 1	.76	2.28	.79	2.37	—	—
Mean.....		2.2		2.27		7.15

TABLE III.

Bottle	Total concentration sulfanilic acid	Resistance				Conductivity $\times 10^6$
1	.05	1736				576.0
2	.01	4175				239.5
3	.005	6234				160.4
4	.0025	9513				105.1
5	.001	17391				57.5
Combination	Ratio	$X \times 10^3$				$K_a \times 10^4$
1-2	2.405	2.321	sulfanilic ion concentration Bottle 2			7.02
1-3	3.591	1.5565	"	"	" 3	7.04
1-4	5.4805	1.021	"	"	" 4	7.05
1-5	10.02	.5576	"	"	" 5	7.03
2-3	1.493	1.5565	"	"	" 3	7.04
2-4	2.279	1.0235	"	"	" 4	7.10
2-5	4.165	.5573	"	"	" 5	7.02
3-4	1.526	1.024	"	"	" 4	7.11
3-5	2.790	.5606	"	"	" 5	7.16
4-5	1.828	.5561	"	"	" 5	6.97
Mean.....						7.05

The value  $7 \times 10^{-4}$  has been used throughout.

One can thus obtain the two equations;

$$\frac{X^2}{C - X} = K, \text{ and } \frac{(rX)^2}{C' - rX} = K$$

which can be solved simultaneously for  $X$  and  $K$ .

Table III gives the values obtained. The water used had a specific conductivity of  $3.5 \times 10^{-6}$  reciprocal ohms, and the temperature was  $21.00^{\circ}\text{C.} \pm 0.02^{\circ}$ , since it was at that temperature that the titration work had been largely carried out.

#### SUMMARY.

From the solubility minimum the value of the basic ionization constant of sulfanilic acid is shown to lie probably between the values  $1.7 \times 10^{-15}$  and  $3.2 \times 10^{-15}$ . From solubility measurements the value of this same constant is shown to lie probably between  $2.0$  and  $2.2 \times 10^{-15}$ , and the isoelectric point of sulfanilic acid is thus at a cH of  $0.056$  or a pH of  $1.25$ . From conductivity ratios the acid ionization constant of sulfanilic acid is shown to be  $7.05 \times 10^{-4}$  at room temperature ( $21^{\circ}\text{C.}$ ).

Calculations are made, from data published in preceding papers, of the ionization constants of glycine,  $K_a$  being  $2.3 \times 10^{-10}$ , and  $K_b$  being  $2.2 \times 10^{-12}$ .

#### BIBLIOGRAPHY.

1. Scudder, H., Electrical conductivity and ionization constants of organic compounds, New York, D. Van Nostrand Co., 1914.